

SURFACTANT ENHANCED FLUID CATALYTIC CRACKING PROCESS

FIELD OF THE INVENTION

[0001] The present invention relates generally to the atomization of fluids. More particularly, the invention is concerned with enhancing the atomization of fluids, especially fluidized cat cracker (FCC) feeds, by using a surfactant to alter the interfacial tension between the fluid and atomizing media.

BACKGROUND OF THE INVENTION

[0002] Atomizing a fluid by passing it through an orifice into a lower pressure zone to produce a spray of droplets is a technique used in a wide variety of applications and processes. For example, in fluidized catalytic cracking (FCC) processes relatively viscous petroleum feeds are converted into more valuable products including gasoline, jet fuel, and heating oil. In a FCC process, a preheated oil feed is mixed with steam and the resulting two-phase fluid is passed into a lower pressure atomization zone in which the oil is atomized and brought into contact with a particulate, hot, cracking catalyst whereby the feed is converted into lower boiling products.

[0003] The trend in FCC technology has been to use more active catalysts thereby reducing the length of time the feed needs to be in contact with the catalyst. To take advantage of a short contact time, however, the oil needs to be uniformly distributed in the form of small droplets. Indeed, experience has shown that long oil vaporization times lead to higher yields of undesirable, low value products. Additionally, as feeds become heavier the fraction of steam dispersion gas must be increased to facilitate atomization. Many FCC units, however, have limited steam capacity, which constrains their ability to effectively process heavier feeds.

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Considerable effort therefore has been devoted to try to find improved ways for atomizing the oil feed in FCC processes. Examples of such are found in, for example, U.S. Patent 5,289,976, U.S. Patent 5,173,175, U.S. Patent 6,093,310 and U.S. Patent 6,352,639 B2.

[0004] Despite the advances made in atomization hardware, and especially FCC feed injection hardware, it would be an improvement in the art if a way could be found to enhance oil atomization in conjunction with hardware and process constraints.

SUMMARY OF THE INVENTION

[0005] The present invention is directed a surfactant-enhanced atomization process. The process comprises:

- a) mixing an effective amount of at least one surfactant with an atomization fluid to form a first mixture;
- b) injecting said first mixture into a fluidized catalytic cracking feedstream to form a second mixture; and
- c) conducting said second mixture through a feed nozzle.

[0006] In another embodiment, the present invention comprises:

- a) mixing an effective amount of at least one surfactant with an atomization fluid to form a first mixture;
- b) injecting said first mixture into a fluidized catalytic cracking feedstream to form a second mixture;
- c) conducting said second mixture through a feed nozzle into a fluidized catalytic cracking reaction zone, thereby producing droplets of the second mixture and injecting them into the reaction zone; and

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- d) contacting the droplets of the second mixture with a FCC catalyst under effective catalytic cracking conditions in the reaction zone thereby producing at least an FCC product stream comprising at least C₂. dry gas and spent catalyst comprising strippable hydrocarbons.

[0007] In one embodiment of the present invention, the effective amount of the at least one surfactant is that amount sufficient to reduce the amount of C₂. dry gas in the FCC product stream, relative to the amount of C₂. dry gas in the FCC product stream in the absence of the surfactant.

[0008] In yet another embodiment, the instant invention further comprises:

- a) fractionating said FCC product stream to produce at least a naphtha boiling range product stream.

[0009] In another embodiment of the present invention, the effective amount of the at least one surfactant is that amount sufficient to reduce the amount of C₂. dry gas in the FCC product stream without causing foaming in the FCC unit.

[0010] In yet another embodiment of the present invention, the effective amount of the at least one surfactant is that amount sufficient to reduce the amount of C₂. dry gas in the FCC product stream without causing foaming, haze, or increasing the oxygenate content of the naphtha boiling range product.

BRIEF DESCRIPTION OF DRAWINGS

[0011] Figure 1 is a plot showing the dynamic interfacial tension (denoted as dynamic IFT) of two different surfactants in water.

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[0012] Figures 2 and 3 show plots of mean droplet diameter vs. steam weight % for oil and steam additized with a surfactant (squares) and oil and steam with no additive (diamonds).

DETAILED DESCRIPTION OF THE INVENTION

[0013] The present invention is directed a surfactant-enhanced fluid catalytic cracking process. In the practice of the present invention, an effective amount of at least one surfactant is mixed with an atomization fluid to form a first mixture. The first mixture is subsequently injected into a fluidized catalytic cracking ("FCC") feedstream to form a second mixture, which is conducted through a feed nozzle. In one embodiment of the present invention, the invention further comprises conducting the second mixture through a feed nozzle into a fluidized catalytic cracking reaction zone, thereby producing droplets of the second mixture and injecting them into a reaction zone. In the reaction zone, the droplets of the second mixture are contacted with a FCC catalyst under effective cracking conditions to produce at least an FCC product stream and spent catalyst comprising strippable hydrocarbons.

[0014] As stated above, in practice of the present invention, an effective amount of at least one surfactant is mixed with an atomization fluid to form a first mixture. Any surfactant that can reduce the static and dynamic interfacial tension between an FCC feedstream and an atomizing fluid may be used. Preferred surfactants suitable for use in the present invention are any of those surfactants known to be thermally stable under feed preheating but will decompose under the effective cracking conditions used herein. Preferably, the at least one surfactant does not contain components containing sulfur, nitrogen and metals. Non-limiting examples of suitable surfactants include non-ionic surfactants and mixtures thereof having

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hydrophilic lipophilic balance values (HLBs) in the range of about 3 to about 20. Non-limiting examples of such surfactants include alkyl alkoxylates, preferably alkyl ethoxylates, mixtures of aldehydes and ketones, preferably alkyl aldehyde acids and ketones, more preferably alkyl aromatic aldehydes and ketones and acids.

[0015] The atomizing fluid may comprise subcooled water (water having a temperature above its normal atmospheric pressure boiling point at pressure sufficient to maintain it in a liquid state), steam, light hydrocarbon gas (C₄-), inert gases and/or combinations thereof. Light hydrocarbon gases include, but are not limited to methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane and butenes and combinations thereof. Inert gases as used herein include, but are not limited to, helium, hydrogen, nitrogen, argon, and other suitable inert gases and combinations thereof. It is preferred that the atomizing fluid be steam.

[0016] The first mixture, i.e. the mixture of surfactants and atomizing fluid, may be prepared either by any one or a combination of methods. Non-limiting examples of preparing the first mixture include adding the surfactant to the atomizing fluid, vaporizing the surfactant and introducing the vaporized surfactant into the atomizing fluid, and adding the surfactant to water and heating the surfactant solution to provide a steam and surfactant mixture.

[0017] If steam is the atomization fluid, alkyl alkoxylate type surfactants are particularly suitable at treat rates in the range of about 25 ppm to 50,000 ppm based on the weight of steam, and preferably in the range of 50 to 10,000 ppm. Especially preferred are alkyl alkyloxylates represented by formulae I to III:

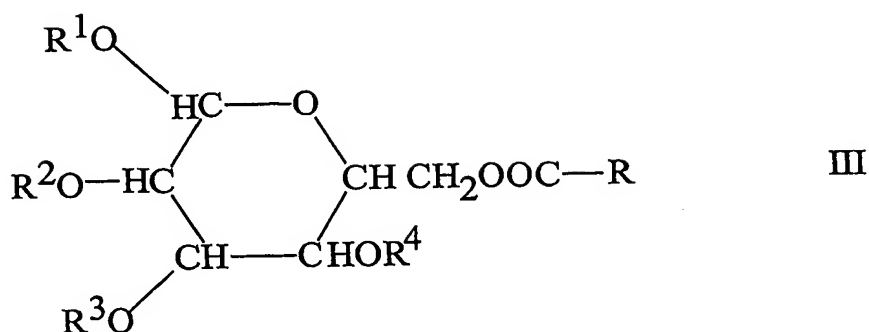
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I



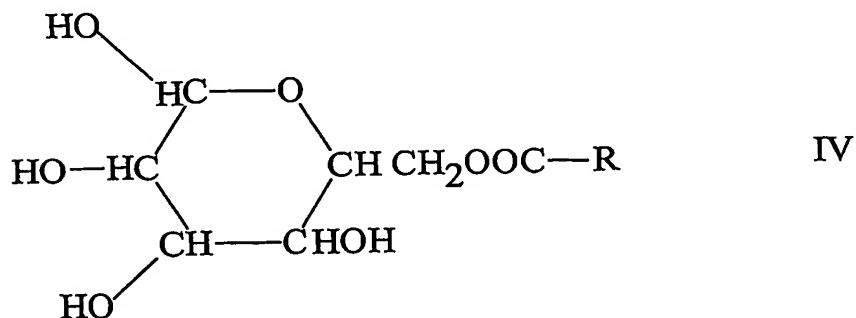
II



III

where R is a linear or branched alkyl group of about 3 to 24 carbon atoms; R^1 , R^2 , R^3 and R^4 are independently alkoxy groups, $(\text{R}^5\text{O})_m\text{H}$ where R^5 is an alkylene group of about 2 to 4 carbon atoms and m is from about 1 to 20, preferably from about 1 to 15, more preferably about 1 to 5, and more preferably about 1 to 3.

[0018] When surfactants have a formula according to surfactant III above are used, it is preferred to use it in combination with an alkyl sorbitan of structure IV.



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[0019] For the alkyl sorbitan it is preferred R is an alkyl group of 3 to 24 carbon atoms. When used in combination with surfactant III the ratio of surfactant III/IV is preferably between about 95/5 to 30/20 and more preferably about 80/20 to 30/70 and even more preferably 75/25 to 50/50.

[0020] It should be noted that any surfactants of the type I, II, III and IV discussed above may be used, alone or in mixtures. It should also be noted that in some instances, an FCC feedstream containing a suitable surfactant can also be used. In this embodiment, when the FCC feedstream is provided with the surfactant or mixture of surfactants, the amount of surfactant generally is in the range of 50 to 20,000 ppm based on the weight of the FCC feedstream, preferably in the range of 50 to 5,000 ppm. Alternatively, a petroleum oil containing alkyl substituted 1, 2 and 3 ring aromatic compounds may be oxidized to generate a suitable mixture of oxidized products suitable as additives for the invention. The oxidization is conducted by heating the oil from about 150°C to about 200°C, in the presence of air for a time sufficient, typically about 4 hours, to produce the oxidized products suitable as additives for the invention. Typically such oxidation produces aldehydes, ketones and acids.

[0021] In the practice of the present innovation, the first mixture is subsequently injected into a fluidized catalytic cracking feedstream to form a second mixture. The method of injecting the first mixture into the FCC feedstream is not critical to the instant invention and can be accomplished by any means known for injecting an atomizing fluid into a hydrocarbonaceous material. Non-limiting examples of suitable injection methods include mixing tees, spargers, and injection devices.

[0022] Any conventional FCC feed can be used in the present invention. Such feeds typically include heavy hydrocarbonaceous feeds boiling in the range of about 430°F to about 1050°F (220-565°C), such as gas oils, heavy hydrocarbon oils comprising materials boiling above 1050°F (565°C); heavy and reduced petroleum crude oil; petroleum atmospheric distillation bottoms; petroleum vacuum distillation bottoms; pitch, asphalt, bitumen, other heavy hydrocarbon residues; tar sand oils; shale oil; liquid products derived from coal liquefaction processes; and mixtures thereof. The FCC feed may also comprise recycled hydrocarbons, such as light or heavy cycle oils.

[0023] As stated above, an effective amount of a surfactant is mixed with an atomizing fluid to form the first mixture that is injected into the FCC feedstream. As used herein, an effective amount of a surfactant is to be considered that amount of surfactant capable of reducing the static and dynamic interfacial tension between the FCC feedstream and atomizing fluid. In a preferred embodiment, an effective amount of surfactant is about 25 to about 50,000 wppm, based on the atomization fluid, more preferably about 25 to about 10,000, most preferably about 25 to about 5,000. Reducing the interfacial tension results in a narrow distribution of small droplets of the second mixture when it is conducted through the feed nozzle. Small droplet sizes increases the vaporization rate of the second mixture and provides better contacting with catalysts. For example, a 25% reduction in the mean oil droplet diameter boosts vaporization rate by 35% to 50%, and shorter vaporization times typically improve the yield of desirable products. Thus, it is preferred that an effective amount of surfactant be that amount effective at reducing the static and dynamic interfacial tension between the FCC feedstream and atomizing fluid by at least 50%. Preferably, an effective amount of surfactant or mixture of surfactants will be that amount sufficient to reduce the static and dynamic interfacial tension

between the FCC feedstream and atomizing fluid such that the droplets formed by conducting the second mixture through a feed nozzle have a mean droplet diameter less than about 1000 μ , preferably less than 500 μ .

[0024] In one embodiment of the present invention, the above-described second mixture is conducted through a feed nozzle into a fluidized catalytic cracking reaction zone. The droplets of the second mixture, having the above-described droplet size, are contacted with a FCC catalyst under effective catalytic cracking conditions in the reaction zone. In this embodiment, any FCC cracking catalyst can be used. Effective cracking conditions include: (i) temperatures from about 500°C to about 650°C, preferably from about 525°C to 600°C; (ii) hydrocarbon partial pressures from about 10 to 40 psia (70-280 kPa), preferably from about 20 to 35 psia (140-245 kPa); and, (iii) a catalyst to feed (wt/wt) ratio from about 1:1 to 12:1, preferably from about 4:1 to 10:1, where the catalyst weight is the total weight of the catalyst composite. The contacting of the second mixture and the FCC catalyst produces at least an FCC product stream comprising at least C₂- dry gas and spent catalyst comprising strippable hydrocarbons. It should be noted that C₂- dry gas as used herein is meant to refer to the gasses produced by the FCC cracking reaction that have a chemical makeup and boiling point range of C₂ and below, i.e. methane, ethane, H₂, C₂= such as ethylene, etc. Thermal cracking produces increased amounts of dry gas while effective catalytic cracking produces less C₂- dry gas than thermal cracking. An efficient FCC produces lower amounts of C₂- dry gas by promoting increased catalytic cracking and decreased thermal cracking. Thus, the efficiency of the present process is noted by a reduction in C₂- dry gas in the FCC product stream. In this embodiment, an effective amount of surfactant is further to be considered an amount of surfactant sufficient to reduce the amount of C₂- dry gas in the FCC product stream.

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[0025] As discussed above, another embodiment of the instant invention involves fractionating the FCC product stream to produce at least a naphtha boiling range product stream. As used herein, a naphtha boiling range product is meant to refer to hydrocarbon streams boiling in the range of about 50°F (10°C) to about 450°F (232°C). The method by which the FCC product stream is fractionated is not critical to the instant invention, and any type of fractionation known can be used. For example, atmospheric or vacuum distillation may be employed in fractionating the FCC product stream. In this embodiment an effective amount of surfactant is further defined as that amount of surfactant sufficient to reduce the amount of C₂- dry gas in the FCC product stream without causing foaming, haze, or increasing the oxygenate content of said naphtha boiling range product stream. Controlling the haze, etc. of the naphtha boiling range product stream is important because it is typically used as a blending component for motor gasolines. It should be noted that haze is typically a result of water entrapment in the naphtha boiling range product.

[0026] Also, as discussed above, another embodiment of the instant invention an effective amount of surfactant is further defined as that amount of surfactant sufficient to reduce the amount of C₂- dry gas in the FCC product stream without causing foaming in the FCC process unit.

[0027] The above description is directed to several embodiments of the present invention. Those skilled in the art will recognize that other embodiments that are equally effective could be devised for carrying out the spirit of this invention.

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[0028] The following examples will illustrate the improved effectiveness of the present invention, but are not meant to limit the present invention in any fashion.

EXAMPLES

[0029] The effectiveness of using a surfactant in the atomization fluid of a Fluidized Catalytic Cracking ("FCC") unit was tested in a nominal 20 kB/D unit. For a period of five days, a surfactant was added in various treat rates under a combination of conditions and with a variety of feeds in order to determine the effect the surfactant would have on the FCC process. The Examples below represent the five days that the surfactant was added to the atomization steam of the FCC.

EXAMPLE 1

[0030] Neodol 91-2.5E, a primary alcohol ethoxylate surfactant commercially available from Shell Chemicals was added to atomization steam in an amount of 1000 wppm, based on the atomization steam mass flow rate. This surfactant-enhanced atomization steam was used to atomize an FCC feed whose properties are listed below:

Gravity, API	19.1
Carbon, wt%	84.7
Hydrogen, wt%	11.57
Nitrogen, wppm	1504
Sulfur, wt%	2.964
5% / 50% / 95% BP (wt)	516 / 798 / 990°F

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[0031] The injection of additized steam continued for a period of 2 to 3 hours. During this test period the FCC unit was operated under constant conditions including an oil feed rate of 16.9 kbbbl/day, 3.7 klb/hr atomization steam, riser outlet temperature of 1005°F, and a catalyst to oil weight ratio of 9.5 lbs. catalyst/lb. of oil.

[0032] During the test run, FCC dry gas samples obtained from the FCC unit were analyzed by gas chromatography, and light cat naphtha ("LCN") having a nominal boiling point range of C₅ - 320°F was collected and analyzed for foaming, haze, and oxygenate content by ASTM D-4815 and confirmed by GC/MS analysis. These analyses showed low ppm levels of alcohols and ketones at the detection limit and virtually the same in LCN samples before and after surfactant addition. The foaming test was conducted by vigorously shaking about 100 ml of the LCN in a 150ml tube for 3 minutes. The agitated LCN was allowed to stand for 1 minute and the initial foam height and time of foam collapse (foam stability) were determined. Base line samples with no surfactant and samples obtained during surfactant addition showed no difference in foam height or foam stability. The LCN was analyzed for haze by visual examination of the sample. Base line samples with no surfactant and samples obtained during surfactant addition showed no difference in haze. A sample of the FCC feed (containing the surfactant-enhanced atomization fluid) was also analyzed by for interfacial tension. About a 5% reduction in each hydrogen, ethane, and ethylene in dry gas samples was observed during the surfactant addition period.

EXAMPLE 2

[0033] The same Neodol 91-2.5E primary alcohol ethoxylate surfactant used in Example 1 was added to atomization steam in an amount of 2000 wppm, based on the steam mass flow rate. This surfactant-enhanced atomization fluid was used to atomize a FCC feed with the following properties:

Gravity, API	19.0
Carbon, wt%	86.41
Hydrogen, wt%	11.73
Nitrogen, wppm	1510
Sulfur, wt%	2.92
5% / 50% / 95% BP (wt)	513 / 796 / 991 °F

[0034] The injection of additized steam continued for a period of 2 to 3 hours. During this period, the FCC unit was operated under constant conditions including an oil feed rate of 16.9 kbbbl/day of feed, 3.7 klb/hr atomization steam, riser outlet temperature of 990°F, and a catalyst to oil weight ratio of 9.5 lbs. catalyst/lb. of oil.

[0035] During the test run, FCC dry gas samples obtained from the FCC unit were analyzed by gas chromatography, and light cat naphtha ("LCN") having a nominal boiling point range of C₅ - 320°F was collected and analyzed for foaming, haze, and oxygenate content. The foaming, oxygenate content, and haze were determined according to the methods outlined in Example 1 above. A Sample of the FCC feed (containing the surfactant-enhanced atomization fluid) was also analyzed for interfacial tension. About 5% reduction in each methane, ethane, and ethylene in dry gas samples was observed during the surfactant addition period.

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EXAMPLE 3

[0036] The same Neodol 91-2.5E primary alcohol ethoxylate surfactant used in Example 1 was added to atomization steam in an amount of 5000 wppm, based on the steam mass flow rate. This surfactant-enhanced atomization fluid was used to atomize an FCC feed with the following properties:

Gravity, API	18.7
Carbon, wt%	85.1
Hydrogen, wt%	11.67
Nitrogen, wppm	1663
Sulfur, wt%	2.979
5% / 50% / 95% BP (wt)	511 / 804 / 1003 °F

[0037] The injection of additized steam continued for a period of 2 to 3 hours. During this test period, the FCC unit was operated under constant conditions including an oil feed rate of 16.9 kbbbl/day of feed, 3.7 klb/hr atomization steam, riser outlet temperature of 990°F, and a catalyst to oil weight ratio of 9.5 lbs. catalyst/lb. of oil.

[0038] During the test run, FCC dry gas samples obtained from the FCC unit were analyzed by gas chromatography, and light cat naphtha ("LCN") having a nominal boiling point range of C₅ - 320 °F was collected and analyzed for foaming, haze, and oxygenate content. The foaming, oxygenate content, and haze were determined according to the methods outlined in Example 1 above. A Sample of the FCC feed (containing the surfactant-enhanced atomization fluid) was also analyzed for interfacial tension. About 5% reduction in each hydrogen, ethane, ethylene, propane, and propylene was observed during the surfactant addition period.

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EXAMPLE 4

[0039] Span 80, Tween-80, Brij-35, Brij-58 and Brij-700 surfactants were used to additize water. Span, Tween and Brij are trademarks of ICI Americas, Inc. The chemical structure of the Brij, Tween and Span surfactants is the same as formula II, III and IV respectively as previously given.

[0040] The air/water equilibrium interfacial tension of a 0.1 wt% solution of the surfactants in water was determined for each surfactant by the Wilhelmy plate method at 25°C. The corresponding air/water equilibrium interfacial tensions are shown in Table 1. A substantial reduction in interfacial tension (from 72 dyne/cm for untreated water) was achieved.

TABLE 1

<u>BRIJ</u>	<u>R</u>	<u>m</u>	<u>HLB</u>	IFT (dyne/cm) <u>(+/- 1)</u>
35	C12	23	16.7	31
52	C16	20	15	42
700	C18	100	18.8	49
<u>TWEEN</u>				
80	C18	$R_1 + R_2 + R_3 + R_4 = -(\text{CH}_2\text{-CH}_2\text{O})_{20}\text{-H}$	15	41
Span 80	C18			

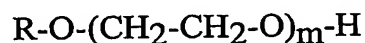
Interface: Air/Water

[0041] The dynamic interfacial tension of Tween 80 in Brij 58 in water was determined by the differential bubble pressure method and the results are shown in

Figure 1. Within two seconds the equilibrium interfacial tension is reached for both surfactants.

EXAMPLE 5

[0042] Neodol 91-2.5E, a surfactant which is a trademark of Shell Chemicals was used to additize water. The chemical structures of the surfactant is shown below:



Neodol: R = linear C₉H₁₉, m = 2

[0043] The FCC feed oil/water interfacial tension at 2000 ppm treat rate of Neodol in water was determined by the pendant drop method at 176°F (80°C)) (Table 2). At least 70% reduction in interfacial tension was observed for the Neodol additive.

TABLE 2

<u>Feed</u>	<u>IFT {+/-1} (dynes/cm)</u>
FCC Feed Oil / Water	20
FCC Feed Oil / 1000 ppm Neodol 91-2 in water	6

EXAMPLE 6

[0044] Two distilled water samples, one containing 1000 ppm of Neodol 91-2.5E and the other 1000 ppm of Exxal DDA-3 were prepared. Exxal DDA-3 is a trademark of ExxonMobil Chemicals with formula I where $n = 3$ and R is branched $C_{12}H_{25}$ group. The samples were heated to 212°F (100°C) with vigorous mixing to produce steam. Steam was collected and condensed in a receiving vessel. Surface tension was measured on the distilled water containing 1000 ppm surfactant and on the condensed water in the receiving vessel. Surface tension of water was 72 dynes/cm. Values of surface tension lower than 72 dynes/cm indicate the presence of surfactants in water. Identical surface tensions for the distilled water containing 2000 ppm surfactant and for the condensed water in the receiving vessel indicate that the surfactants vaporize with steam. The results are shown in Table 3.

TABLE 3

<u>Feed</u>	<u>IFT {+/- 0.5} (dynes/cm)</u>
Water	72
1000 ppm Neodol in water	25.6
Condensed water in receiving vessel	26.8
100 ppm Exxal DDA-3 in water	25.6
Condensed water in receiving vessel	27.6

EXAMPLE 7

[0045] FCC feed atomization experiments were conducted to determine the influence of oil additization and steam additization on droplet size. In the case of oil additization, the oil was additized with a Tween 80/Span 80 mixture in the ratio of 60/40 at a treat rate of 2000 ppm based on the weight of oil. The oil with additive was preheated to 150°F (66°C). The preheated oil was passed through a calibrated rotameter at 3 g/sec, and further heated to 450°F (232°C). Superheated steam at 450°F (232°C) was produced using a flash vaporization heater. The water inlet to the flash vaporization heater was monitored using a rotameter.

[0046] The superheated steam and oil was mixed in a T-junction, and passed through a feed injector, 120 mm long and 1.4 mm in diameter. The pressure and temperature of the oil and steam mixture were monitored at the T-junction using a thermocouple and a pressure gauge. The oil and steam mixture was sprayed horizontally into an exhaust system, which separated the oil from the steam.

[0047] A Malvern particle diameter analyzer was positioned 3 inches from the exit of the feed injector. Drop sizes were obtained at each operating condition for three separate runs. Good repeatability between the runs was observed. The flow rate was maintained within +/- 2% during the duration of data collection. The temperature was also maintained within +/- 2°C during the same period. Figure 2 shows the results, namely a reduction in droplet size.

[0048] In the case of steam additization, Neodal 91-2.5E was added to water at a treat rate to produce 2000 ppm of Neodol based on the weight of steam, the water heated to produce a mixture of steam and additive and the mixture was then mixed

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with the oil in a T-junction. Thereafter the procedure as with oil additization was followed.

[0049] The effect of the Neodol steam additive on the Sauter Mean Diameter (SMD) (SMD = diameter of liquid oil droplet with the same volume/surface ratio as the entire spray) of drop sizes is shown in Figure 3. A 5-10% reduction in oil droplet SMD was obtained with Neodal additization of steam.

EXAMPLE 8

[0050] 200 g of a crude oil from western Canada was placed in a three-necked glass flask and heated to a temperature of 150°C to 180°C for 4 hours with a continuous purge of air at 80 to 100 scf/bbl/hour. After completion of reaction the product was tapped hot from the reactor. The product was added to n-decane at various concentrations and mixed. Equilibrium oil/water interfacial tension was determined using the pendant drop described in the art. Results are shown in Table 4.

TABLE 4

<u>Wt% AO Product</u>	<u>Interfacial Tension dynes/cm</u>
None	56
0.1	22
1	25
10	30

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For all concentrations of product added to n-decane, a substantial decrease in interfacial tension was observed, which is forecast to correspondingly improve atomization of the liquid hydrocarbon.